SILICONE VAPOR POISONING OF CATALYTIC METHANE SENSORS

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ABSTRACT

Various silicone materials have been proposed for use in mining environments. The catalytic methane sensors now employed are poisoned by silicone vapors. Activated charcoal and carbon cloth adsorbents will increase the sensor lifetimes in an environment containing significant silicone vapor concentrations. The results of a study of catalytic methane sensor operation with adsorbent materials in hexamethyldisiloxane-air mixtures are reported. Sampling techniques developed for measuring silicone vapor content of mine atmospheres are described.

INTRODUCTION

The Code of Federal Regulations Title 30, section 75-300, administered by the Mining Safety and Health Administration (MSHA), Department of Labor, requires methane gas concentration monitoring in coal mines. Such monitoring is used both as a measure of mine atmosphere flammability and as a criterion for ventilation adequacy. Methane (CH_4) action levels are set at less than 0.25 % CH_4 for use of air from nonworking areas, less than 1% CH_4 for permissible work areas, greater than 1% CH_4 for increase in ventilation, and greater than 2% CH_4 for automatic deenergizing of machinery operating at the coal face. Thus accurate and reproducible methane sensors are mandated to insure productive and safe coal mine operation.

Methane measurement by the use of catalytic methane sensors is used currently in most of the methane monitors and detectors underground. With this sensor methane is catalytically oxidized in air on finely divided platinum (Pt) or palladium (Pd) ceramic surfaces. The resulting heat of combustion increases the temperature of the surface and of an inner platinum wire spiral. The methane concentration in air is proportional to the resistance increase of the inner platinum wire. The catalytic methane sensor was developed in Great Britain by the Safety in Mining Research Establishment (SMRE) and has an excellent record of accuracy and stability for measuring combustible gases such as methane in mines as long as there is an adequate oxygen supply (greater than 10%) and absence of several specific poisons for the catalytic surface.

The catalytic methane sensors using Pt or Pd catalysts are poisoned--suffer a loss in response--when brought in contact with several classes of chemicals. Manufacturers' literature and earlier reported studies list several of these chemicals (table 1). In general, compounds that react with Pt or Pd metals to form highly stable metal compounds--sulphides or phosphates--are poisons as well as silicones and lead oxide film formers. Organic halides are strongly adsorbed and are classed as temporary poisons. Although such poisons for catalytic methane sensors have been identified for some time, they did not become a problem during mining operations until lately when the commercial use of silicones or phosphate esters became more common.

Silicone compounds may be used in the mining industry in many commercial preparations. These include grease formulations, silicone rubbers, hydraulic fluids, heat transfer fluids in transformers and capacitors, oils, and water emulsions for polishes, waxes, and aerosol sprays.

Silicone compounds in these formulations consist mostly of linear dimethyl siloxane polymers. They are produced by three sources in the U.S.--Dow Corning[1], General Electric, and Union Carbide. The poly dimethyl siloxane fluids have several unique properties:

Wide fluid or liquid range, -50°C to 100°C
Viscosity range dependent on molecular weight, 0.6 cs to 10^6 cs
Extreme stability to thermal degradation or oxidation at high temperatures, stable at 200°C in air
High surface wettability.

Selected physical properties of the linear dimethyl siloxane polymers with trimethyl siloxane terminal groups are summarized in table 2. The number of silicon atoms in polymers may extend to

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[1] Use of name brands is for identification only and does not imply endorsement by the Bureau of Mines.

over several thousand for high-viscosity materials. Hexamethyldisiloxane is the lowest molecular weight species in the series and has the greatest vapor pressure. Silicone fluids have molecular weights from 300 to 1,000. More viscous liquids used in antifoam preparations range from 40,000 to 100,000 molecular weight units or 1,000 to 30,000 centistokes (cs) viscosity. Polishes and lubricants range from 100, to 5,000 cs viscosity, and gums used in rubber compounding are cross-linked to form the largest and stiffest compounds. The vapor pressure for the polymer system and the concentration of silicone vapor saturated in air is greater than 0.01 ppb for molecular weights of 977 or less. Commercial preparations of high-molecular-weight silicones are not pure compounds; molecular weights quoted are a number average, and some systems may contain small quantities of low-molecular-weight species which may be expected to volatilize during use. Commercial specifications for high-viscosity systems state less than 2% loss in weight on volatilization at 200 °C for 48 hours.(9)* This weight loss may consist of volatile silicone species or some entrained moisture. Silicone compounds in commercial preparations may be composed of silicones other than the dimethyl siloxane system replacing some of the methyl groups with phenyl, hydrogen, or halogen atoms, resulting in compounds with greater volatility and increased reactivity.

Silicone rubbers are composed of high-molecular-weight cross-linked systems and would be considered nonvolatile in finished form. However, if the rubber were to contain unreacted monomer or partially reacted short polymers, or if the rubber is of the room temperature volatilization (RTV) type and is still fluid and not completely set, then volatile silicone compounds will be present and in sufficient quantity could form poisons for catalytic sensors. RTV rubbers liberate acetic acid when reacting with atmospheric moisture to form reactive Si-OH groups. Systems in common use may involve reaction of methyl triacetoxy silane monomer with poly dimethyl siloxane α,w diols to form a cross-linked product.

The boiling point of methyl triacetoxy silane is 90° at 9 mm Hg pressure. An estimate of vapor pressure at room temperature is 1.8 mm Hg or 2,400 ppm concentration in saturated air. Until RTV silicone is fully polymerized, this compound may poison catalytic methane sensors.

Silicon plastics, resins, and two-component rubbers that have been heat-cured would be expected to have negligible volatile silicone concentrations. The vapor pressure of low-molecular-weight silicone linear compounds may be expressed by the following equation dependent on temperature and polymer length (number of silicon atoms):

$$\text{Log } p = 6.59 + 0.47n - \frac{972}{T} - \frac{392.2n}{T} \quad (10)$$

where p = vapor pressure, mm Hg
t = temperature absolute, °K
and n = total number of silicon atoms in molecule.
The constants were recalculated from more recent data.(8)

* Numbers in parenthesis refer to References at the end of the paper.

The saturated silicone concentration in air is calculated from the vapor pressure

$$C = \frac{P_s}{P} \times 10^6$$

where C = ppm silicone
P_s = silicone partial pressure, mm HG
and P = total atmospheric

EXPERIMENTAL WORK

A summary of previous work on effects of poisons on catalytic methane sensors has been presented in a series of papers by Jack Firth and Allan Jones of SMRE, Great Britain. (1)(7)(14) Unprotected and charcoal-protected sensors were poisoned with hexamethyl disiloxane (HMDS) in air-CH_4 mixtures, and loss of sensitivity of the palladium sensor to methane and other combustible gases was studied. The results of the test of poisoning of sensors by HMDS are summarized in table 3. The table includes poison effects noted for dimethylsiloxane polymer and triethyl phosphate as well. The times for poisoning reported were from 10 seconds to 10 minutes for losses in response from 12 to 50%. The shorter poisoning times were measured using direct impingement of reactive gases on the portable catalytic methane-sensing unit. The longer times noted were for poisoning effect of machine-mounted sensors which incorporate stainless steel screens and heavy porous sintered metal filters for mechanical protection and flame safety (fig. 1); these times reflect the time for diffusion of silicone vapor through the diffusion barriers and adsorption of poison on the porous metal surface. The use of activated charcoal for adsorbing the poisons before contact with the sensors was extremely effective, increasing life of the sensors by 240 times.

In this study two combustible gas detectors, one with palladium and one with platinum sensors, were tested for susceptibility to silicone poisoning with HMDS and with RTV silicone rubber fluids.

The poisoning of the catalytic methane sensors was monitored by observing the sensor response to methane during administration of a silicone-air mixture. The catalytic sensors were mounted in the top of an acrylic cylinder for initial tests and housed in an aluminum cylinder in later work. The test apparatus is represented in figure 2. The methane test gas was diluted to 2% (and 1%) concentration in a mixing tube; concentration was measured by periodic readings from a Riken methanometer by gas refractive index measurement. The methane concentration was intermittently varied from 2% concentration to 0% concentration by control of a solenoid valve run by a mechanical timer. Pulse times ranging from 6 minutes air and 6 minutes 2% methane to 50 minutes air and 10 minutes 2% methane were used in testing. The gas samples were purified by passage through an activated charcoal filter before introduction into the silicone vapor generation chamber.

Silicone vapor was generated by bubbling on air-CH_4 mixture through a fritted disk immersed in HMDS cooled to 0°C by ice in a Dewar vacuum container. The slicon vapor concentration was formed by using a fixed ratio of bypass air to airflow through the silicon bubbler and was calculated as follows:

$$C \text{ Silicone in air-}CH_4 \text{ mix} = \frac{P_s}{P} \frac{V_{\text{silicone flow-air}} \times 10^6}{V_{\text{total flow}}}$$

where C = concentration in ppm silicone
P_s = 8.6 mm Hg for HMDS at 0°C
P = total air pressure, 750 mm Hg normal
V_{silicone} = air-CH_4 mix flow rate through silicone bubbler, ml/min
and $V_{\text{total flow}}$ = total air-CH_4 mix flowrate, ml/min.

Total flow rates were measured on a wet-test volume meter, noting volume measured in a given time period. Silicone vapor generator airflow was measured using a standard soap bubble meter measuring time of bubble transit through a calibrated volume. The mixed air-silicone-CH_4 flows were introduced into the test chamber containing the catalytic methane sensors with methane response measured on a strip chart recorder. Determination of the silicone vapor concentration was initially performed by absorbing the silicone in 100 ml of methyl isobutyl ketone (MIBK) using two bubbler absorption columns in series. For runs of 30-minute duration, the second absorption column contained 1/7 the concentration of the first, and handling, cleaning, and refilling the scrubbers was time consuming. Activated-charcoal tubes containing CAL Calgon charcoal were used to monitor silicone vapor composition in test gas in later experiments. All of the silicone adsorbed was confined to the first 1-cm bed tube; HMDS concentration was 54 ppm, and the solid tubes were convenient to use.

Adsorption experiments were conducted with very low concentrations of HMDS in air by the use of diffusion tubes (fig. 3). HMDS contained in a 200-ml flask was connected to an upper flask with glass tubing of fixed diameter and length. The upper flask had inlet and outlet tubes for diluent airflow. HMDS vapor moved from the lower flask to the upper flask through the tube by diffusion. The vapor pressure of the HMDS was determined by holding the flask at a fixed temperature, either 0°C or -63°C, by external refrigeration of fluid in a Dewar vacuum container.(15) It was found that gas flow through the upper flask must be constant since oscillation of pressure caused by air from a diaphragm pump increased the rate of material transport by convection many times over the rate calculated for diffusion. The concentration of silicone in air produced by use of the diffusion tube was monitored by adsorbing silicone on activated charcoal in a tube, and analysis for adsorbed silicone was conducted after the test.

Analysis of the MIBK absorption liquid or of the activated charcoal tubes after extraction of adsorbed silicone (HMDS) by MIBK was performed using atomic absorption (AA) spectrometric measurement. The silicone solution in MIBK was aspirated into a nitrous oxide-acetylene flame at high flow rate, and the silicon optical absorption was determined at 2516 A° using a 2 A° slit width on a Perkin-Elmer Model 503 unit. Standard solutions were made by dilution of a weighed HMDS solution in MIBK. Standard analyses were also made with a solid octaphenyl cyclotetra siloxane weighed sample dissolved in MIBK.[13] Standard curves constructed with experimental optical density plotted versus weight-percent silicone were linear.

Hexamethyl disiloxane was chosen as catalyst poison for this test since it could be obtained in pure form; it is very volatile, boiling at 100°C, and since it is a small molecule, it is not as easily adsorbed on charcoal as larger molecules. In addition to experiments with HMDS, tests with both Dow Corning and General Electric RTV silicone rubber fluids were conducted.

Sensor poison tests with RTV silicone rubber fluid (before solid formation) were performed by extruding 1-1/4-inch lengths of silicone at each end of a polyethylene 3/4-inch-OD tube. The air-2% CH_4 mixture was passed through the tube and over the sensor on test. Vapor pressure of silicone in RTV rubber fluid was measured by flowing a known volume of air through sample tubes with 1-1/4-inch lengths of RTV silicone rubber fluid and adsorbing the vaporized silicone onto a CAL charcoal bed 1 cm thick in another tube. Thirty-minute runs were conducted at flow rates from 1 to 1.1 l/min with fresh RTV silicone added at 15-minute intervals. The charcoal test samples were analyzed for silicone content after extraction of adsorbed silicone with MIBK by the previously described AA technique.

DISCUSSION

The ability of silicone compounds to poison catalytic methane sensors depends on the volatility of the silicone and on transport of the silicone-air mixture by air currents to the sensor. Because of ventilation requirements in coal mines--3,000 cfm airflow minimum into the working area--formation of 5 ppm silicone vapor concentration would require vaporization and mixing of 3 grams of silicone compound per minute. Low-molecular-weight silicone compounds in fluids or as impurities in high-molecular-weight viscous systems may yield significant silicone volatile species from commercial products or by depolymerization during use. Only by tests of the poisoning ability of commercial mixtures can the actual volatile silicone content or ability to poison a sensor be ascertained.

Initial experiments in poisoning of catalytic methane sensors were performed with HMDS as poisoning agent at 54 ppm concentration in air and in air-2% CH_4 mixtures. Platinum and palladium sensor methane monitors were tested with and without CAL charcoal over the sensor to remove silicone vapor by adsorption. The time response for methane indication during poisoning is presented in figure 4. A 10% loss in response was obtained for both sensors in 15 minutes without protection. With a 2-mm thickness of CAL charcoal protecting the sensor, runs were obtained for 10% loss in response in 42 hours and 144 hours for palladium- and platinum-type sensors, respectively. Although the silicone concentration in the air inlet to the test chamber was 54 ppm, initial values of 18 to 22 ppm silicone obtained from the chamber exit air show significant adsorption by the chamber contents: four sensors, two coatings of CAL charcoal, four sintered-metal flame suppressors, and the chamber walls.

Experiments on platinum sensor methane monitors were conducted at very low levels of HMDS generated by a diffusion tube held at -63°C by mechanical refrigeration. The average assault concentration of HMDS during test was 5.5 ppb. The concentration of HMDS ranged from 16 ppb initially to 3.77 ppb in the final test, and 4,000- to 7,900-minute tests were made to obtain enough HMDS on each series of CAL charcoal sample tubes for AA analysis. The response of the monitors was measured in series for the HMDS measurement, and breakthrough of the low concentration of HMDS vapor was noted on two tests for these very long trapping times.

Silicone vapor poisoning of catalytic methane sensors may be delayed by adsorption on activated charcoal surrounding the sensor elements. The thicker the layer of charcoal, the longer the sensor can operate without being poisoned. The thicker layers of charcoal cause a longer sensor response time. Practical methane sensors require rapid response as well as protection from poison, so there is a limit to the thickness or adsorbent material that can be used. For a response time of 1 minute or less the maximum adsorption layer thickness allowed is 2mm for this sensor.

Tests previously conducted used times of sensor response loss in methane as a measure of protection offered by a given adsorbent. Possible protection effect may also be assessed for a material by measuring the amount of adsorption of silicone vapor on a known amount of absorbent. The adsorption isotherms for HMDS on various charcoal substitutes were measured by equilibrating the test substrate with known concentrations of HMDS in air, and the amount of HMDS adsorbed was measured after extraction into MIBK with analysis by AA spectrometry.

An adsorption isotherm for HMDS on CAL charcoal is presented in figure 5. The amount of HMDS adsorbed can be determined from this figure for known concentrations of silicone vapor in air. Although more HMDS is adsorbed at high concentration, sufficient HMDS is still adsorbed at low concentrations to protect sensors. Saturated (77°F) values of HMDS adsorption for various carbon materials can be used to screen possible adsorbents, and equilibrium values are listed in table 4 for dry air-HMDS systems. In terms of total quantity of HMDS adsorbed, the following preference in substrate is indicated: CAL, PCB, MDA cloth, CDE cloth (20 cal/gm heat of wetting with benzene).

CONCLUSIONS

Catalytic methane sensors are poisoned rapidly by volatile silicone materials, confirming early work performed by SMRE, Great Britain, and manufacturers' literature. Once a catalytic methane sensor in use in a mine is poisoned by silicones or related poisons, the instrument may incorrectly indicate safe methane concentrations when possibly high concentrations, in explosive range, are present. Silicone compounds may be incorporated in transformer coolants, hydraulic or brake fluids, lubricants, sealants, waxes, polishes, and other mixtures available or intended for use in mines.

Volatile silicone compounds or other poisonous agents should not be introduced into mine atmospheres when methane detectors or monitors are in use, unless appropriate steps are taken to assure that harmful monitor or detector poisoning does not occur. Should it be suspected that such a silicone has been introduced into a mine immediate steps should be taken to test each methane detector or monitor to ascertain performance accuracy using known methane-air[12] mixtures. Silicone-containing materials may be identified by labeled contents listing, or by chemical analysis for silicon by wet chemical, emission spectroscopic, or AA spectrometric techniques. The presence of volatile silicone compounds in a mine atmosphere may be tested by adsorption of the silicone vapor on a CAL activated charcoal 1-cm-thick trap using a permissible air sample pump to deliver a 1- to 4-l/min flow rate. The adsorbed silicone can be eluted into MIBK and analyzed for silicone content by the AA technique described.

Protection of catalytic methane sensors by adsorption of poison before contact with the sensor element is practical for low concentration levels of silicones. Thin layers of adsorbent on diffusion heads are necessary for protection so that minimum effect will be obtained on response times.

The Mine Safety and Health Commission of the European communities has proposed the use of a layer of activated charcoal cloth covering the sensor element for protection of handheld methane detectors. The use of such protection may become mandatory in Great Britain, France, and Germany, for example, requiring demonstration of protection of handheld methane detectors against 5 ppm HMDS concentrations in air-CH_4 mixtures for a test time of 1 to 2 hours without loss in response greater than 10%. Regular maintenance of such units is recommended, including replacement of the charcoal cloth during maintenance checks every 2 to 4 weeks.

It is recommended that manufacturers of catalytic methane sensors, recognizing the increased importance of protection from poisoning with the proposed use of new mining compounds, would market such protective devices to prevent poisoning of the sensors by attachment of an adsorbent to the present diffusion-type methane monitor or detector. Manufacturers should recommend also a maintenance program with periodic replacement of adsorbing materials to assure device reliability.

This study has focused attention only on the use of adsorbents to remove poisons from contact with catalytic methane sensors. It is also possible that suitable oxidation catalysts may be developed to react with poisons to form nonpoisonous products that will give a longer protective life and require less frequent replacement.

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Table 1.--Catalytic methane sensor poison classes

Compound	Structure	Reference
Organic Halides.....	R-X X = Cl, Br, I	1, 4, 5, 6, 7
Silicone.....	$R-\left(\begin{matrix}CH_3\\Si-O\\CH_3\end{matrix}\right)-R$	1, 2, 3, 4, 5, 6
Phosphate.....	$R-OP-(O\ R)_3$	1, 6
Metal.....	$Pb-(C_2H_5)_4$	1, 3, 4, 5, 6
Sulfide.....	R_2-S	4, 5, 6
Other.....	H_2SO_4 (mist) HCN Cl_2 SO_2	6 7

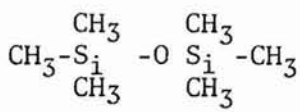
TABLE 3.--Catalytic methane sensor poisoning effects

Material	Life	Life, charcoal protected	% Response	Reference
MS 200/10 silicone oil.....	5 min	20 hr	20/2% CH_4	SMRE data
Triethyl phosphate.....	5 min	20 hr	15/2% CH_4	do.
Hexamethyl siloxane (HMDS), 26 ppm.....	26 sec	22 hr	33/1% CH_4	do.
HMDS, 40 ppm.....	10,30 sec	-	50	14
HMDS, 54 ppm.....	10 min* 8 min**	 167 hr* 99 hr**	12 12 25 50	Present work

* Pd sensor
** Pt sensor

TABLE 2.--Properties of linear dimethyl siloxane polymers

Silicon atoms N	Viscosity, cs	Molecular weight	Vapor pressure, mm Hg at 25°C	Equilibrium concentration air, ppm at 25°C
2	0.65	162	37.00	48,700
4	1.50	310	0.96	1,260
6	3.0	439	0.04	52
13	11.	977	10^{-8}	.013
130	100.	10,000		
400	1,000.	40,000		
1,000	12,500	90,000		
1,200	30,000	100,000		
1,900	500,000	143,000		

N = 2  Hexamethyldisiloxane

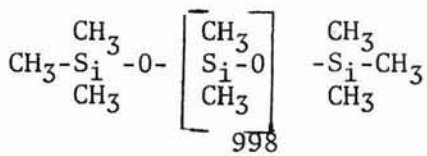
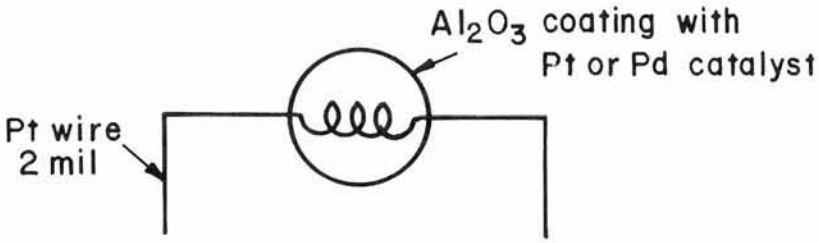
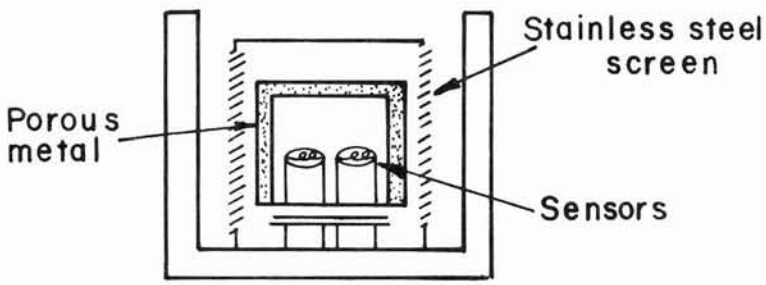
N = 1000 

TABLE 4.--Equilibrium adsorption of HMDS by charcoal substrates, 25 to 27 °C

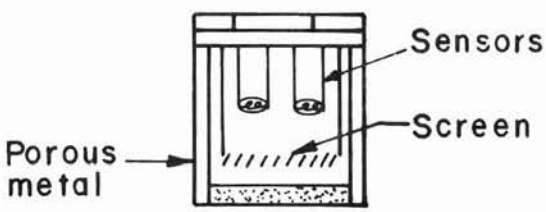
Substrate	HMDS adsorbed per g charcoal, mg
Granular:	
CAL, Calgon	331, 347
BPL, Calgon	311
PCB, Calgon	340
WVG Nuchar, Westvaco	288
WVH Nuchar, Westvaco	274
PC1333, Barneby-Cheney	159
Foam carbon:	
RVC 4X5 80A, Chemotronics Intl	33
Cloth:	
CC-2, MDA Scientific	265, 271
Chemical Defense Establishment, Great Britain:	
1	21
5	18
10	157
20	203



Catalytic sensor



Pt sensor head



Pd sensor head

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FIGURE 1.--Catalytic Methane Sensors

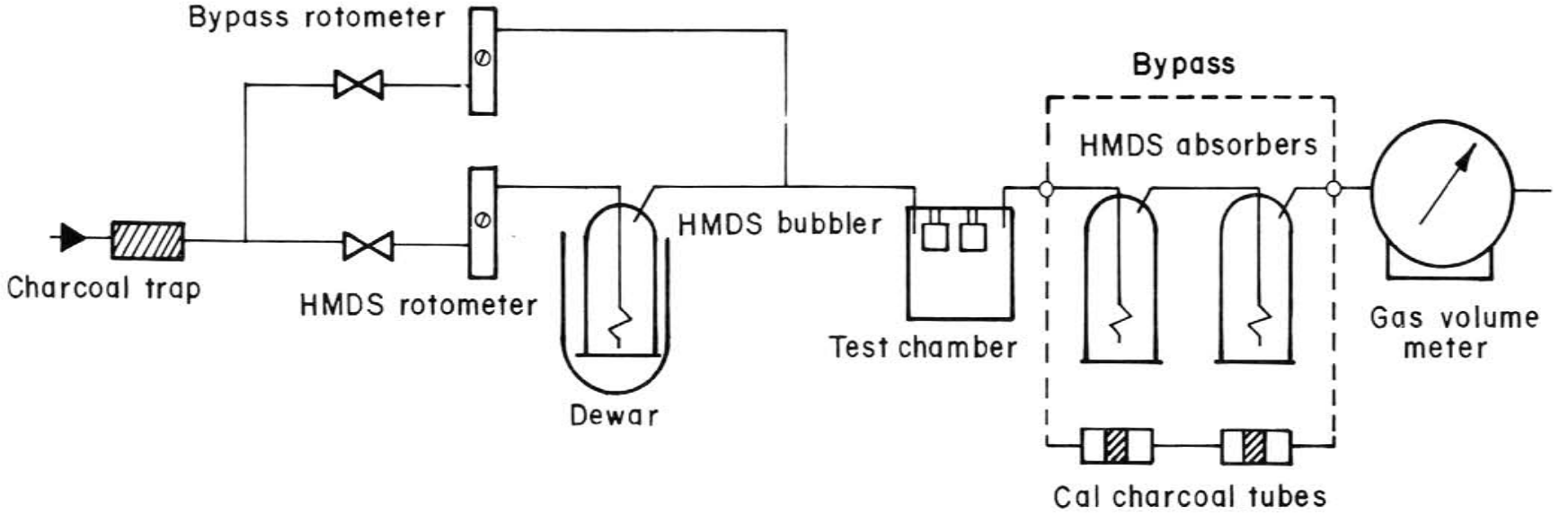

FIGURE 2.--Catalytic Sensor Test Apparatus

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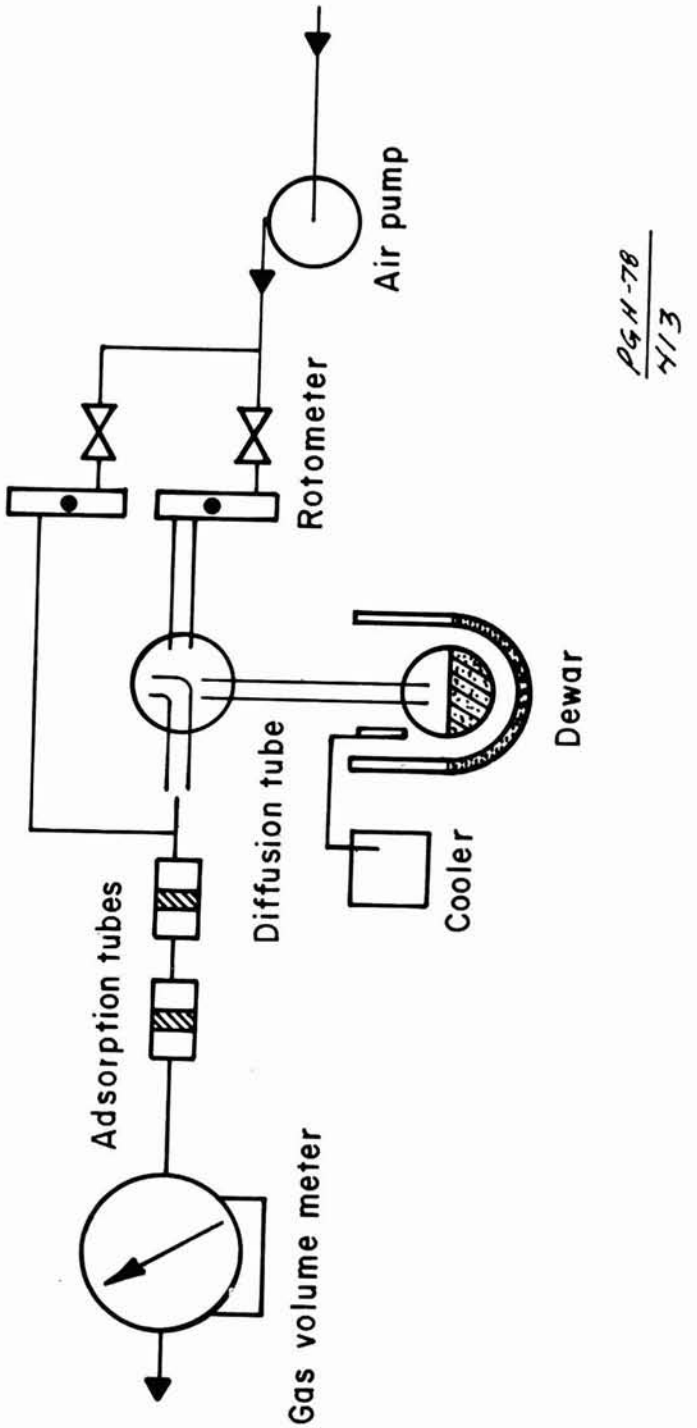

FIGURE 3.--Diffusion Tube Apparatus.

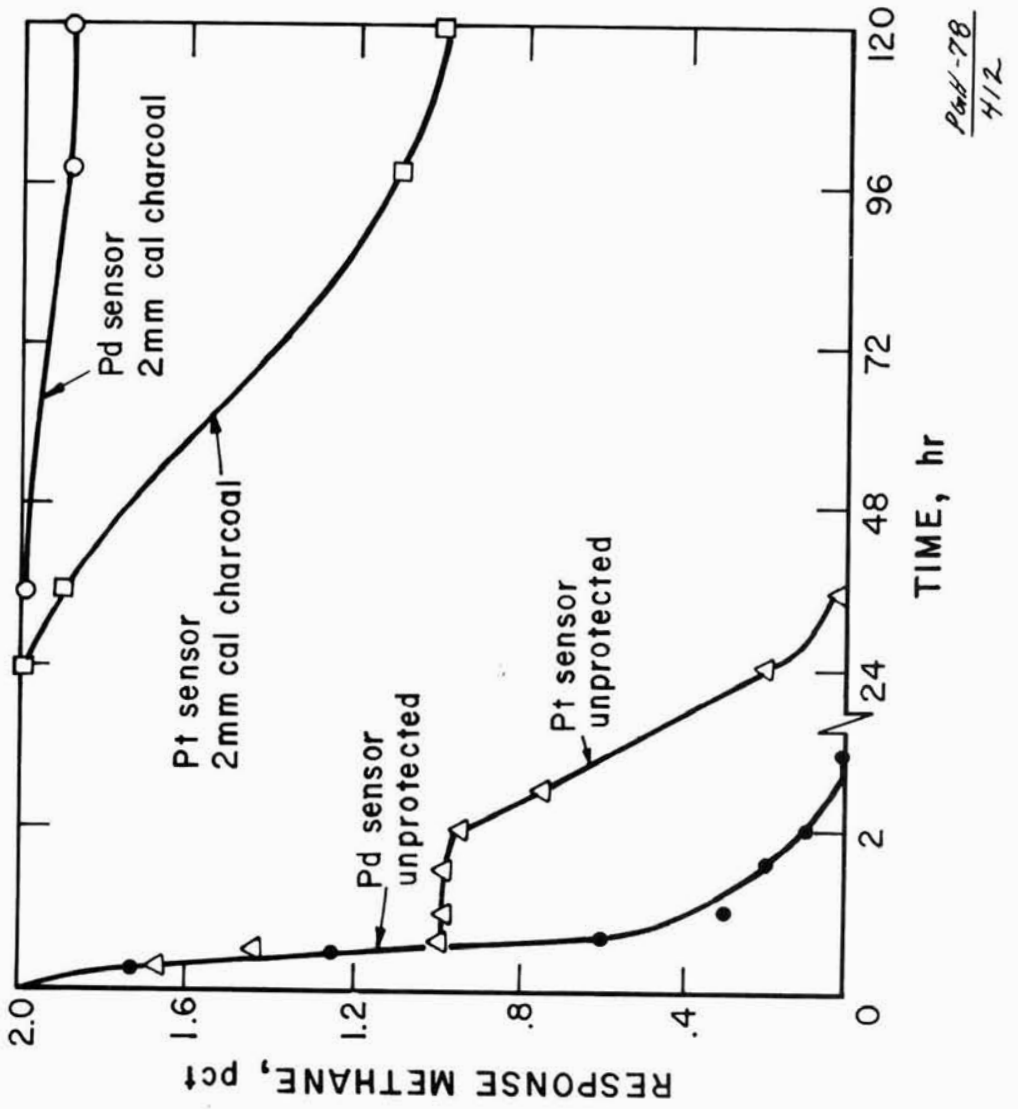

FIGURE 4.--54 ppm Hexamethyldisiloxane Poisoning of Catalytic Methane Sensors

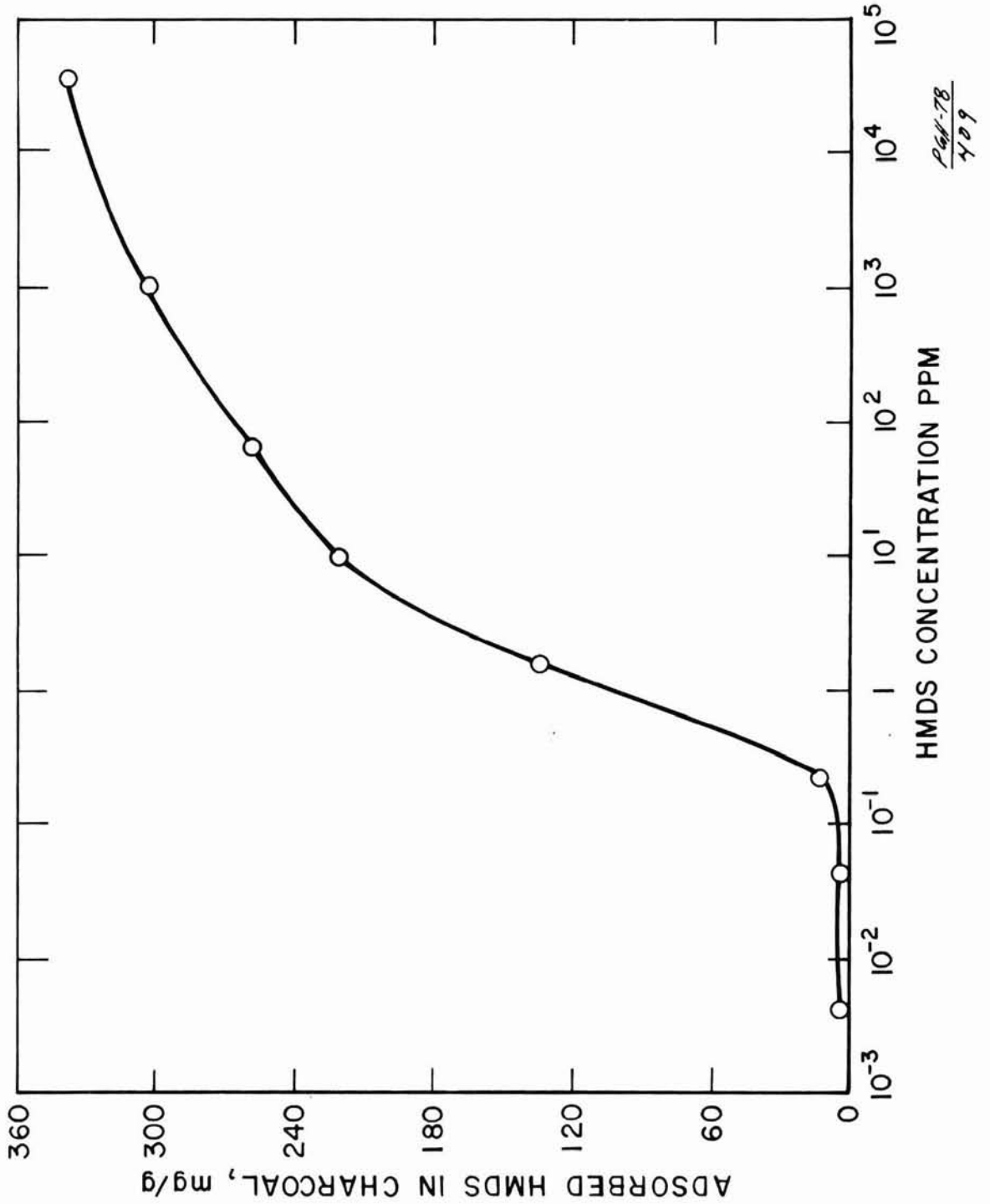

FIGURE 5.--Adsorption Isotherm Hexamethyldisiloxane. 77 °F